THE ESTIMATION OF THE ATOMIC WEIGHT OF THE CALCIUM CONTAINED IN A VERY OLD POTASSIUM-RICH ROCK OCCURRING AT RHICONICH, NEAR CAPE WRATH, SUTHERLANDSHIRE.

Thesis for the Degree of Ph.D.

Presented by

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CONTENTS

The Atomic Weight of the Calcium contained in a very old potassium-rich rock occurring at Rhiconich, near Cape Wrath, Sutherlandshire.

INTRODUCTION:-

When, in 1903, it was pointed out by Schuster that every property belonging to one element had later been found to be shared by the others in varying degrees, there were made numerous attempts to measure the radioactive disintegrations of substances other than those of the well known radioactive families, and although at the outset apparent confirmation for Schuster's suggestion was forthcoming, it was later found that the rays emitted by common subatances under examination could be traced to the presence of minute quantities of one or more of the real radio-active elements. From this work it was concluded that the common elements did not undergo radioactive transformation, but in 1906, Campbell and Wood (Proc. Camb. Phil. Soc. 14, 15, 1906) discovered that two exceptions, potassium and rubidium, could be found to this general rule. In both cases the radioactivity was very feeble, but it was proved beyond doubt that the disintegration was a property of the potassium and rubidium atoms alone. The radiation is a β-radiation and no α-rays have been detected. Measurements on the rate of emission of the β-rays made it possible for Holmes and Lawson (Phil. Mag. 2, 1218, 1926) to estimate, on the

assumption that every potassium atom was radioactive, the half value period for potassium as 1.5×10^{12} years.

Potassium however consists of two known isotopes of masses 39 and 41, and Hevesy (Nature, 120, 838, 1927), who recognized the fact that one of those isotopes (or possibly a third unknown isotope) might be responsible for the β-radiation, investigated the problem by attempting a partial separation of the potassium isotopes by means of the "ideal" distillation method. The heavy fraction had for its atomic weight a value 0.005 unit higher than that of ordinary potassium. Biltz and Ziegert (Phys. Zeit. 29, 197, 1928) measured the activity of this fraction and found it to be greater than that of ordinary potassium by 4%, a result which is in accordance with the supposition that the heavier isotope, K_{41} is mainly, if not solely, responsible for the β-radiation. Now this isotope 41 only constitutes about $\frac{1}{20}^{th}$ of the element, so that the half value period is lowered to 7.5×10^{10} years. Recently is has been suggested by Muhlhoff, (Ann. Phys. 1930 (v) 7, 205-224) and also by Hevesy, Seith and Pahl, (Zeit. Phys. Chem. Bodenstein Festband pp. 309-310) that the half value period of 1×10^{12} is more probably correct, but contradiction to this point of view is to be obtained from the work by Allison. (Phys. Rev. 40, 1015, 1932)

Since the emission of a β-particle results in a one unit increase in the nuclear charge, it follows that an isotope of calcium, Ca_{41}, should be produced as a result of the radioactive disintegration of K_{41}. Only the calcium isotopes 40 and 44 have been recognized experimentally, but it is a matter of real significance that the determination of the atomic weight of the calcium obtained in a very old potassium rich mineral of small initial calcium content, might establish the existence of this isotope Ca_{41}, for if the potassium content is high it is possible that enough of the isotope K_{41} will have disintegrated to raise the final atomic weight of the calcium above the normal value of 40.08.

Allison, by a new magneto-optic method for the detection of isotopes, found a minimum in light intensity, corresponding to Ca_{41}, between Ca_{40} and Ca_{44} when the substance under examination was sylvine, and the presence of this minimum with only six samples from a total of fourteen of commercial calcium salts proved that a third isotope of ordinary calcium could not be responsible for the minimum. Surprisingly high results for the percentage of Ca_{41} in potassium minerals furnished the suggestion that the half value period advanced by Holmes and Lawson is of the correct order, but there is not yet general

acceptance of Allison's figures.

Two direct attempts have been made to detect the increase in the atomic weight of the calcium contained in potassium rich minerals. A.V. Frost and O. Frost, (Nature, 175, 48, Jan. 1930) secured a microcline from Miask containing 11 per cent of potassium and .042% calcium, and from this they extracted 0.15gm. CaO. After purification by repeated percipitation as sulphate and oxalate, atomic weight determinations from the ratio $CaCl_2$: $CaBr_2$ yielded the values 40.21 and 40.24. Parallel experiments with ordinary calcium gave the values 40.06, 40.16, and 40.08 for the atomic weight, and from these results it was claimed that an increased atomic weight had been observed, Objection to these figures was, however, made by Hönigschmid and Kempter, (Zeit. Anorg. Chem. 195, 1, 1930) on the ground that the values for ordinary calcium made it impossible to regard with trust the method of purification, and it was shown from their subsequent research that the method could be made satisfactory only when larger amounts of starting material allowed of the sacrifice of nine tenths during the purification.

Hönigschmid and Kempter reinvestigated the problem of an increased atomic weight using as starting material a preparation of calcium obtained from sylvine. Parallel experiments with ordinary

calcium, where the method of purification was that recommended by Richards and Hönigschmid (Jour. Amer. Chem. Soc. 32, 12, 1910) gave as the atomic weight 40.085 ±.0006. The sylvine calcium was still further purified by two precipitations as oxalate, and two samples of this calcium gave average atomic weights of 40.194 and 40.226. It was discovered however that strontium was present as impurity, and to remove this strontium repeated precipitations as oxalate - the only effective method - were made. A redetermination of the atomic weight yielded the value 40.093 and spectroscopic examination showed that strontium was not present in sufficient quantity to raise the result beyond the experimental error.

From these results Hönigschmid and Kempter were unable to draw any conclusion with regard to the presence or absence of Ca_{41}, but there still remained the possibility that the selection of a very much older potassium mineral than sylvine, with a high potassium and a small calcium content, might provide sufficient Ca_{41} to raise the atomic weight above the normal. The geological age of sylvine is of the order 2×10^8 years, which is comparatively young, as there are many mineralogical formations about 1000 to 1500 million years old. As the amount of Ca_{41} in a potassium rock

increases with the geological age it is obvious that the detection of Ca_{41} by an atomic weight determination will be assisted if the rock is of great age. A felspar rock, about 1000 million years old, containing about 9.35% K_2O and 0.27% CaO, was located at Rhiconich, near Cape Wrath, Sutherlandshire, and has been used for the present research.

ANALYSIS OF ROCK

(Geological Survey, " Summary of Progress for 1919," p.p.43-44.)

SUBSTANCE	PERCENTAGE
SiO_2	72.10
TiO_2	Trace
Al_2O_3	15.14
Fe_2O_3	0.63
FeO	0.05
MnO	0.06
CaO	0.27
MgO	0.03
K_2O	9.35
Na_2O	2.05
H_2O (+105°)	0.05
H_2O (-105°)	0.21
P_2O_5	0.10

EXPERIMENTAL:-

For the determination of the atomic weight of calcium either of the two methods adopted by Richards in his classical researches may be employed. Briefly these are as follows. Pure calcium chloride contained in a platinum boat is fused first in an atmosphere of hydrochloric acid and then in an atmosphere of nitrogen. After cooling and weighing the fused salt is dissolved in water and its deviation from neutrality measured, using methyl red as indicator. For the method in which the amount of chlorine present in the solution is determined by the weighing of silver chloride, excess silver is added, but for the nephelometric method, only the equivalent amount of silver is added. It was shown byRichards and Hönigschmid (Jour. Amer. Chem. Soc. 32, 12, 1910) that this latter method is more accurate and simple, and this is the one which has beenadopted in the present research. The details of this method will be given in that part of the thesis devoted to the experimental procedure.

PREPARATION OF PURE MATERIALS:-

The use of pure materials throughout the research is a point of paramount importance, and accordingly, all the solid, liquid and gaseous reagents were purified with greatest care.

(a) WATER:-

Large amounts of pure water were required, and for its preparation a five litre pyrex glass flask fitted with a ground-in condenser and ground-in receiver was used. The best laboratory water, of conductivity about 1.5×10^{-6} r.o., was distilled with baryta and potassium permanganate to remove carbon dioxide and organic matter. The distillate was rejected whenever its conductivity rose above 1×10^{-6} r.o. This water was good enough for most purposes and it was stored in stoppered Jena glass bottles which for many years had only been employed for keeping the best conductivity water. For the final recrystallisations of calcium nitrate and calcium chloride, and for the final nephelometric tests, the water was distilled immediately before use through a quartz condenser.

(b) NITRIC ACID:-

A.R. nitric acid was distilled with small quantities of barium nitrate and silver nitrate to remove possible traces of sulphate and chloride. The head and tail fractions were rejected and the middle fraction was redistilled. This process was twice repeated, the head and tail fractions being each time rejected. A Pyrex glass flask with ground-in condenser was employed for the distillations.

(c) HYDROCHLORIC ACID:-

Constant-boiling A.R. hydrochloric acid, containing a few crystals of potassium permanganate to remove bromine and iodine, was slowly distilled from a pyrex flask fitted with a ground-in condenser. The middle fraction was twice redistilled, once through pyrex and once through quartz, and each time the head and tail fractions were rejected.

(d) AMMONIUM OXALATE:-

About 2000 gms. of A.R. ammonium oxalate were four times recrystallised, Twenty grams of the pure material gave no residue when heated in a platinum crucible.

(e) AMMONIUM CARBONATE:-

A cold saturated solution of A.R. ammonium carbonate was slowly run into boiling water contained in a flask fitted with a quartz condenser. By regulation of the entering solution, and by rapid cooling of the condenser, it was possible to make the distillate almost a saturated solution.

(f) CALCIUM OXIDE:-

A.R. calcium nitrate was dissolved in water and boiled with lime to remove traces of iron which might be present as impurity. The solution after filtration through a sintered Jena Glass Gooch crucible was acidified with nitric acid and the nitrate then three times recrystallised. The calcium nitrate was then

converted into carbonate by the addition of ammonium carbonate and the pure dry carbonate was then packed into a large porcelain boat and heated at about 1100 in an atmosphere of pure hydrogen. Before heating, the surface of the carbonate was made into a series of depressions, and in this way there was prepared a boat of lime suitable for the fusion of small silver buttons.

(g) AMMONIUM FORMATE:-

A.R. formic acid was twice distilled through quartz, the middle fraction only being collected. Pure ammonia, made by heating a concentrated solution of A.R. ammonia, was dissolved in water, and the solution, on addition to the formic acid, gave the required ammonium formate.

(h) HYDROGEN:-

A.R. Zinc, free from arsenic and antimony, was treated with pure hydrochloric acid. The hydrogen was purified by passing it through silver nitrate solution, copper sulphate solution, two towers of soda lime, and finally through a tube containing P_2O_5

(i) SILVER:-

The problem of the preparation of pure silver has been an important one in many atomic weight determinations, but its successful solution was first accomplished by Richards and Wells (Carnegie.Inst. Wash. Publ. 28) in their investigations on the atomic

weights of sodium and chlorine. Silver metal can be made pure in many ways but the difficulty arises in eliminating mother liquor etc., while preparing the metal in a form suitable for weighing. Fusion of the metal was early recognized to be the only safe method of removing entirely the mother liquor contained in the silver crystals, whether these had been prepared either by electrolysis or by chemical reduction. Stas, in his work, recommended the fusion to be conducted in an atmosphere of hydrogen on a cupel of basic calcium phosphate, but the inherent defect in this method, namely the probability of contamination of the silver with phosphorus, led Richards and Wells to investigate others which might be free from similar objection, and they ultimately selected one which had been employed by Stas very early in his career. Many preliminary experiments revealed that silver fused on pure lime in an atmosphere of hydrogen, to remove dissolved oxygen, was of very great purity.

The gas furnace used for the fusion of the silver consisted of a silica tube about 2 feet long and $2\frac{1}{2}$ inches wide, round which was fitted a circular container of asbestos formed into shape by moistening, wrapping round a Winchester bottle and slow drying at 100°. In this way the slow drying gives a very durable container which shows little tendency to split or

crack under the intensive heating required for the fusion of the silver. The ends of the tube were made gas-tight by luting on filter funnels with paste of moist lime of a consistency such that the hardening of the paste due to the expulsion of water by the heating was not accompanied by fracture of the joint. One end of the tube was at an angle to the horizontal axis so that the filter funnel could be luted on to provide a window convenient for observing the progress of the fusion. The boat containing the silver was placed on a layer of asbestos paper from which all volatile matter had been removed by a previous baking out of the furnace.

A.R. silver nitrate was recrystallised eight times and dissolved in water to which was then added a hot solution of pure ammonium formate till reduction was complete. The white precipitate of silver was many times boiled with pure water, and then dried at 300° for about an hour. The depressions in the lime boat were filled with silver and the boat placed in the furnace. After all the air had been swept out the heating was commenced and the progress of the fusion was observed through the window. The silver was maintained in the molten condition for twenty minutes in the atmosphere of hydrogen, and after cooling it was etched with pure nitric acid to remove adhering lime.

The clean buttons were boiled many times with pure water, dried at 400° for six hours, and kept

in a dessicator over solid caustic potash.

A sample of silver was also prepared in the same way from the residues of the sixth recrystallisation of the silver nitrate.

BALANCE AND WEIGHING:-

The balance used in the research was a Kuhlmann microanalytical balance with a beam of 70 mm. and a maximum load of twenty grams. Owing to the circumstance that the three knife edges were parallel and lay in the same plane the sensitivity remained practically constant with changing load, and by following the method recommended by Richards it was possible to standardize the weights with an accuracy of ±.005 milligram. The balance was housed in a sheltered room where the temperature was maintained at 18 ± 0.5°C It was further protected from draughts by being enclosed in a compartment of tin foil and then in a small cardboard house capable of seating the observer. During the preliminary experiments with the balance it early became evident that careful thermal regulation of the room was a matter of supreme importance, for not only did a variation in temperature produce, inside the balance case, air currents causing disturbing effects of serious magnitude, but it also resulted in an alteration of the zero point deflection. The balance was illuminated from a distance of six feet

by a 60 watt lamp enclosed in a box, the aperture of which was shielded by a "cooling" solution of potassium chromate.

All weighings were made by substitution, and as the counterpoises were always similar in size and shape to the object to be weighed, the weights required were never large and consequently changes in the meteorological conditions could be neglected.

In reducing weights in air to weights in vacuo the densities of the various substances had to be taken into consideration. The platinum-brass weights had a density of 8.3 and the corrections for 1 gram of substance weighed in dry air at 18°C and 760 mm. are given in the table below.

Substance.	Density	Vacuum Correction.
Silver.	10.49	-.000032
Calcium Chloride.	2.15	+.000377

The fractional weights were of aluminium of density 2.6 and corresponding corrections were applied at 18°C and 760 mm.

Substance.	Density.	Vacuum Correction.
Silver.	10.49	-.000351
Calcium Chloride.	2.15	+.000097

The wide differences between the densities of brass and calcium chloride and silver and aluminium, made it necessary to record the barometric pressure when silver and calcium chloride were weighed. Graphs were drawn giving these corrections.

EXTRACTION OF CALCIUM FROM THE ROCK AND PURIFICATION OF CALCIUM CHLORIDE FOR ANALYSIS.

During the preparation of pure calcium chloride for analysis the loss of material at each stage in the purification processes is frequently considerable, and in order to obtain about 25 gm. of the final product it was considered necessary to extract from the rock about 80 gm. calcium as element. The rock however, contained only about 0.27% CaO., i.e., 0.20% calcium, so that the extraction of 80gm. necessitated the treatment of at least 90 lbs. rock. The difficulties involved in the sodium carbonate fusion of such large quantities of material were so tremendous, that search was made to discover an extraction process which might prove adaptable to the rock in question.

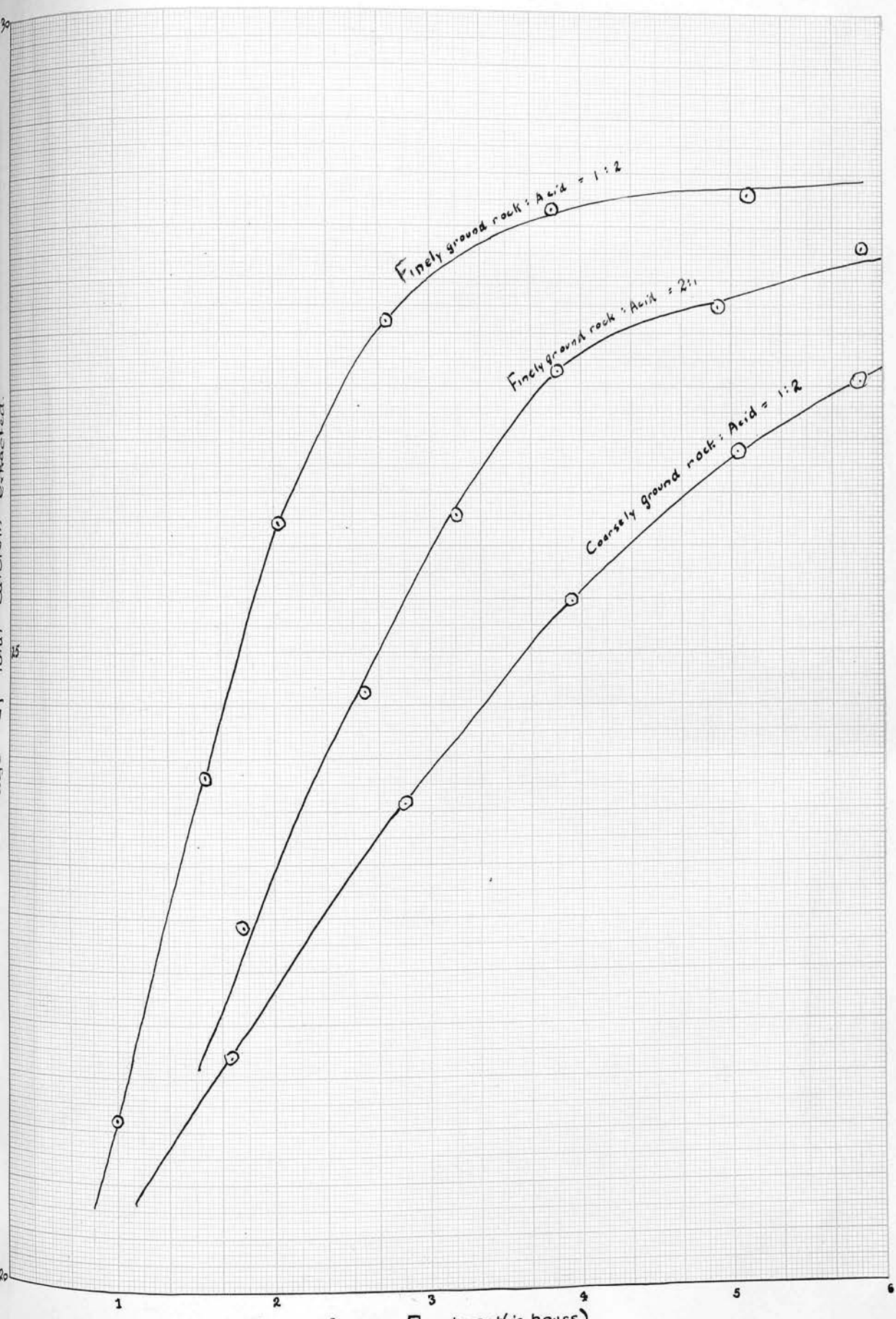
In the patent literature (Blanc, Patent Specifation, 181,677, Feb. 15, 1922. No. 4436/22.) therewas found a method which was claimed by the inventor to be of great success for the extraction of potassium from minerals such as leucite, by the circulation of certain acids through a layer of the material, and it was thought that anacid digestion of the rock might furnish the solution to the difficulty. Test experiments performed with hydrochloric acid, nitric acid, sulphuric acid, and aqua regia revealed that the first mentioned was by far the best for the purpose.

Investigation on the importance of fineness of the grinding was next undertaken, for it was obvious that if coarse particles were freely pervious to the boiling acid, considerable time and labour might be saved. It was found however, that the success of the extraction was most marked in the case of finely ground rock.

Two further points of importance in the extraction of large quantities of rock, namely, the time of treatment with acid, and the Acid:Rock ratio were next studied, and for these 20gm. rock and 40c.c. constant boiling hydrochloric acid were placed in a flask fitted with a reflux condenser. The graph shows the importance of the time factor.

On the small scale extraction it was found that the efficiency was not impaired by reducing the quantity of acid to 10c.c., but on the large scale, where stirring of the contents was impossible, bumping and risk of fracture became serious.

In order to extract the calcium the rock was therefore pulverized in a jaw crusher, ground first in a disc-grinder and then in a ball mill. A series of six five litre pyrex flasks fitted with reflux condensers was set up, and into each were put 4 lbs. finely ground rock and $3\frac{1}{2}$ litres constant boiling hydrochloric acid. After six hours treatment the solution was filtered and evaporated to remove the


Finely ground rock : Acid = 1 : 2
Finely ground rock : Acid = 2 : 1
Coarsely ground rock : Acid = 1 : 2
1
2
3
4
5
6
Time of acid Treatment (in hours).

excess acid which was employed for further extraction of the rock. After dilution, the remaining solution was neutralized with ammonia to remove iron. The filtered solutionwas acidified and any remaining iron oxidised by chlorine gas, after which it was again precipitated by the addition of ammonium oxalate. The extraction was continued until 230 gm. calcium oxalate had been obtained.

The relative efficiency of hydrochloric acid over the other reagents tested during the preliminary experiments was very fortunate for not only did it simplify enormously the problem of removal of the excess acid, but it helped materially towards the proof of the presence or absence of Ca_{41} in the rock, as also did the fact that slightly less than 30% of the total calcium content was extracted. The treatment of rocks with hydrochloric acid is common in the extraction ofpotassium from potassium minerals and as Ca_{41} is formed from potassium it will probably exist in the crystal lattice at a point favourable to attack by acid. Ordinary calcium, present in the rock during its formation, may probably exist in the crystal lattice under entirely different conditions, and as the proportion of calcium extracted during the extraction with acid only increases slowly with time, after four hours treatment, a preferential extraction of Ca must be regarded as a possibility.

The calcium oxalate, in quantities of 20 grams,

was dissolved in boiling dilute hydrochloric acid and slowly precipitated by the addition of ammonia. The total loss in weight in the first reprecipitation of calcium oxalatewas approximately 11 grams, pointing to the removal of magnesium, and possibly barium and strontium if these were present, but in the second and third the loss was very small and largely mechanical. In the fourth stage of the purification the acid was not completely neutralised with ammonia, and the calcium oxalate was allowed slowly to crystallise during the cooling of the large volumes of very dilute acid. About 205 grams of oxalate remained.

In order to obtain a calcium suitable for preliminary and comparative work in the determination of the atomic weight cleaned, selected sea-shells were crushed, incinerated to destroy organic matter, and treated with hydrochloric acid. By a method similar to that mentioned, about 800 gm. of pure calcium oxalate were obtained. Sea shells were chosen as the source of ordinary calcium to obtain what might be called an average representative modern calcium. Calcium minerals, such as leucite, although of comparatively recent origin, might at some time have been in close contact with potassium, and as a result might have been contaminated with Ca_{41} formed by the disintegration of K_{41}. During the formation of the calcium deposit this Ca_{41} isotope

would naturally settle out with the ordinary calcium, and might influence the atomic weight considerably. Within the waters of the oceans however, where the proportion of potassium to calcium would be relatively small, this excessive introduction of Ca_{41} would be prevented, and the marine organisms would therefore build up on "average modern calcium" in which the atomic weight difference would be negligible.

The two quantities of calcium oxalate were incinerated at 700° in platinum basins, and the remaining greyish mass was, after solution in pure nitric acid, filtered through sintered Jena glass to remove the carbon produced during the strong heating. After the dilution of the clear solution so obtained to a large volume and the addition of pure ammonium oxalate, the calcium oxalate produced was well washed with pure water, dried and re-incinerated at 700°C in platinum basins. The almost white residue of calcium oxide was treated with slightly less than the equivalent amount of nitric acid and the faintly alkaline solution boiled and filtered.

A quantity of solution was withdrawn from the main volume and the calcium content precipitated as carbonate by a solution of pure ammonium carbonate. The washed carbonate, after drying and conversion into lime by strong heating in a platinum crucible, was added to the remainder of the solution, which previously had been made slightly acid with nitric acid, and through which chlorine had been slowly bubbled for an hour to oxidise any remaining trace of iron to the ferric state. The alkaline solution was boiled and filtered and the entire process was twice repeated, the small amounts of oxide being each time prepared from the filtered solution. It might be assumed that no iron or magnesium could have remained, but in order to make certain, the slightly alkaline solution was, after boiling with lime, electrolysed with platinum electrodes for six hours, and filtered. From this stage onwards the calcium nitrate was brought into contact only with platinum or silica, and any reagent employed also had been purified in vessels of these materials.

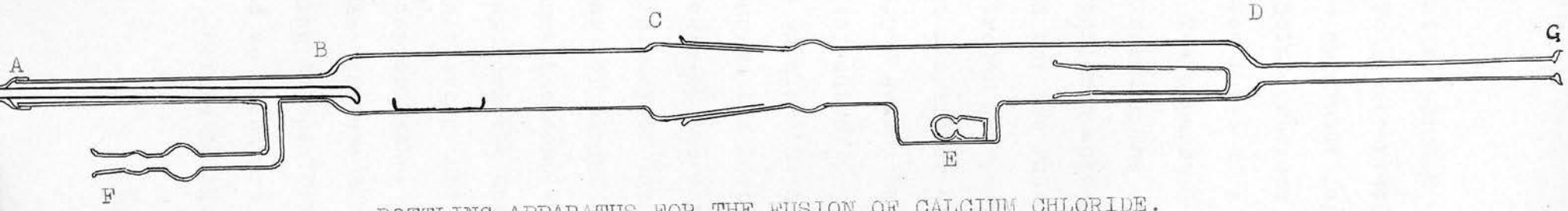
The calcium nitrate was recrystallised five times with thorough draining of the mother liquid, and the nitrates from the fourth and fifth crystallisations were taken for conversion into separate samples of chloride. This was done by precipitating

the calcium from dilute solution as carbonate by the addition of ammonium carbonate, washing the precipitate with boiling water, in a platinum Gooch crucible, and redissolving the carbonate in pure hydrochloric acid. Precipitation and redissolving were twice repeated to ensure the complete removal of nitrate ions, and the final solution of pure calcium chloride was, after filtration through platinum, gently evaporated, The crystals of calcium chloride were kept over fresh pure lime, below 29°, the transition temperature of the hydrated salt, in a dessicator evacuated with a Hyvac pump.

During the crystallisations of the nitrate and the chloride every precaution was taken to exclude dust and impure laboratory air. Heating was conducted electrically and all operations were performed inside a glass house.

MELTING AND WEIGHING OF THE CALCIUM CHLORIDE.

The apparatus employed for the fusion of the calcium chloride was similar to the "Harvard bottling apparatus" of Richards and Wells (loc. cit.). A diagram is given. The part ABCF, constructed entirely of fused quartz, was ground into the pyrex glass tube CD, on which there was blown a short wide side bulb E of a size sufficient to hold the stopper of the weighing bottle situated between the bulb and the narrow end of the tube. A short piece of rubber



BOTTLING APPARATUS FOR THE FUSION OF CALCIUM CHLORIDE.

tubing at A, through which passed a long close-fitting silica rod, prevented, at this point access of air into the apparatus during the fusion, and at F a ground joint provided a means of interchanging absorption tubes of either calcium chloride or soda lime. The apparatus connected at G was so constructed that by turning the correct stop cock an atmosphere of hydrochloric acid gas, nitrogen, or air could be supplied for the fusion.

Nitrogen was prepared by passing the compressed gas from a cylinder over a tightly packed roll of fine copper gauze, two feet long by one inch wide, heated to redness. The issuing gas was bubbled through an alkaline solution of pyrogallol, which not only removed the last traces of oxygen but also served to indicate, by the darkening which occurs on oxidation, the efficiency of the copper in removing the small percentage of oxygen contained in the nitrogen. Throughout the complete range of experiments there was no appreciable darkening of the alkaline pyrogallol solution, proving that all the oxygen had been retained by the copper gauze. When the surface of the gauze was three quarters blackened along the length of the tube, owing to the formation of copper oxide, hydrogen was used to reconvert the roll into bright shining metal. Before being passed into the bottling

apparatus the nitrogen was passed through a series of five towers, the first two of which contained silver nitrate solution and solid caustic potash successively while the last three contained concentrated sulphuric acid. The silver nitrate and sulphuric acid towers were packed with glass pearls to break up the gas into very small bubbles during its passage through the reagents. The nitrogen was finally dried by driving it slowly through a tube containing phosphorus pentoxide.

The hydrochloric acid gas was prepared by dropping concentrated A.R. sulphuric acid into a solution of pure hydrochloric acid. It was shown by Baxter and Hines (Jour. Amer. Chem. Soc. 28, 779, 1906) that phosphorus pentoxide could not be used for the drying of hydrochloric acid gas owing to the formation of volatile compounds of phosphorus, but the gas can be made very dry by passing it over glass beads moistened with freshly distilled sulphuric acid. The apparatus for the generation and drying of hydrochloric acid was constructed entirely of glass to avoid contamination of the gas with organic compounds, and after the generator had been refilled the air in the apparatus was swept out with oxygen-free nitrogen.

The air, which was supplied by a water-blower, was purified by passing successively through wash bottles containing silver nitrate, solid caustic

potash, and concentrated sulphuric acid, and was finally dried by passing over a layer of phosphorus pentoxide 24 inches long.

In detail the procedure was as follows. The partially dehydrated crystals of calcium chloride, which had been kept over good lime in a vacuum dessicator for about six weeks and which were very friable, were carefully transferred with the aid of a silica spoon from the platinum basin to the platinum boat. The boat was placed in the quartz tube and, after the entire apparatus had been connected, a slow stream of nitrogen was driven through for an hour in order to expel all oxygen. The temperature of the quartz tube during the latter half of the passage of nitrogen was maintained at about 400°, so that the chloride was almost completely freed from water. Dry hydrochloric acid gas was then admitted and, when all the nitrogen had been replaced, the temperature was raised to 800°, where fusion of the salt occurred and the last traces of water were driven off. The fusion was maintained for fifteen to twenty minutes in the slow current of hydrochloric acid, and bubbles of gas which formed on the foot of the platinum boat were removed by gentle tapping of the quartz tube with a wooden peg. The hydrochloric acid was replaced by nitrogen and, after the salt had been kept in the molten condition for a further five minutes, the heating was

stopped and the product allowed to cool in the current of nitrogen. The ignition in nitrogen was carried out to prevent the shattering of the chloride and distortion of the platinum boat during the crystallisation of the clear solid.

After cooling, the nitrogen was replaced by dry air, and the boat pushed into the weighing bottle by means of the silica rod passing through the piece of rubber tubing at A. By rotation of the pyrex tube BCF the stopper was gently tilted from the side bulb and pushed into the neck of the weighing bottle. The stopper and weighing bottle had been very finely polished with rouge, so that while standing in a dessicator near the balance for six hours previous to weighing, the fused calcium chloride was maintained in its atmosphere of pure dry air. The counterpoise was filled before each experiment with pure dry air and was allowed to stand in the balance case for some time beside the bottle containing the chloride, near a tube containing radioactive material, so that any electrical changes, which might have interfered with the weighing, could be dissipated.

As a result of fourteen fusions the total loss in weight of the platinum boat was 1.3 milligrams, i.e., an average of 0.09 milligram in a single experiment, but as any platinum which had dissolved in the

fused chloride probably reverted to the metallic condition during the five-minutes strong heating in the atmosphere of nitrogen the initial weight of the boat in each determination was taken as the correct value.

As the fusion of the calcium chloride was known not always to yield an exactly neutral product, it was essential in each experiment accurately to determine the departure from neutrality. This was done by dissolving the weighed chloride in a small amount of pure water in a 250c.c. stoppered pyrex glass flask, and by diluting to the same volume in a similar flask an equal weight of calcium chloride which had been four times recrystallised from water. This chloride was certainly neutral, as there is no evidence that either calcium oxide or hydrochloric acid, is preferentially absorbed when calcium chloride is crystallised from aqueous solution. 10c.c. of a saturated solution of methyl red were added to each flask and the solution of fused chloride was titrated with either dilute nitric acid or caustic potash solution, of a strength equivalent to 1mgm. Cl^- per 10c.c., depending on whether the colour was more red, or more yellow than that of the solution of neutral calcium chloride. On an average the correction was about 0.3mgm. and the titration was correct to within an accuracy of two drops, i.e., 0.00001gm. Cl^-. According as acid or alkali had been employed in the

titration, the corresponding weight of calcium oxide or hydrochloric acid was subtracted from the weight of calcium chloride, for it was assumed that an acid reaction pointed to the presence of dissolved hydrochloric acid while an alkaline one signified the loss of chlorine and production of calcium oxide during the ignition in the atmosphere of nitrogen.

PRECIPITATION AND GRAVIMETRIC TITRATION.

In each experiment with the chloride derived from sea shells the atomic weight of the calcium was assumed to be 40.075, and from the weight of fused calcium chloride the weight of silver required to precipitate the chlorine as silver chloride, was calculated. By the selection of buttons of a suitable size, as nearly as possible the calculated amount of silver was weighed directly on the balance pan and transferred to a one-litre flask fitted with a ground-in condenser having a series of bulbs on the stem. A slight excess of pure nitric acid was added and, after the silver had completely dissolved, the liquid was diluted and boiled to expel nitrous vapours. The liquid was further diluted to about 800cc. and great care was taken to wash spray from the walls of the condenser.

The solution of calcium chloride was transferred to a three litre conical flask with a well polished stopper, and the smaller flask was washed until the

total volume measured about a litre. To this liquid was added from a dilute solution the silver or chloride necessary to adjust the weighed amounts of silver and calcium chloride to the values required for the exact precipitation of silver chloride, assuming the atomic weight of calcium from sea shells as 40.075 and that of calcium from rock as 40.090. The main silver solution was added little by little to the chloride solution in the red light of a dark room, and after the transference of every trace of silver, the conical flask was gently rotated to ensure thorough mixing of the two liquids. At this stage violent shaking of the liquid was avoided to prevent cohesion of the precipitate, which might interfere with the washing-out of occluded silver or chloride. With the very dilute solutions employed the possibility of occlusion was very slight, but it was considered necessary to guard against it. On the following morning the flask was violently agitated for twenty minutes to coagulate the white precipitate of silver chloride. It was shown by Richards and Willard (Publ. Carnegie Inst. 125,31, 1910) that the accuracy with which the end point could be determined by means of the nephelometer was almost inversely proportional to the concentration of silver chloride dissolved in the solution, and accordingly, the flask

was cooled in ice for twenty four hours in the dark room.

As was mentioned above, the exact amounts of silver and calcium chloride were used in the experiments. This was done to enable the nephelometric tests to be carried out in the near region of the end point. It was shown by Briscoe, Kikuchi, and Peel, (Proc. Roy. Soc. 133, 440, 1931) in their redetermination of the atomic weight of thallium, that an alternative to the nephelometric method might be found in the addition of an excess of about 2 mgm. silver to the chloride silution, and the estimation of this excess by titration with N/1000 potassium thiocyanate, using iron alum as indicator. The ease and rapidity of the method, combined with its high degree of accuracy in the thallium experiments where very close agreement was obtained, rendered it necessary to ascertain whether its application could be made with success to the case of calcium. Preliminary experiments revealed that the presence of calcium nitrate in no way interfered with the titration of the silver, but it was found that after the evaporation of the large volumes of solution containing dissolved silver chloride and calcium nitrate, the extremely rapid fading of the colour of the indicator made the estimation of the excess silver somewhat uncertain, and accordingly it became

necessary to revert to the more tedious nephelometric method.

The nephelometer used in the research was constructed by the Klett Instrument Company. Special cups were made, having no vulcanite in contact with the interior, and the plane glass ends of the plungers were fused on to the black glass barrels. A movement of .5 millimetre of one of the cups was sufficient to change the shades of the two half-fields seen through the eye-piece of the instrument.

The stopper of the conical flask containing the clear ice-cold liquid above the coagulated silver chloride was carefully withdrawn so as not to disturb the precipitate, and 10cc. of the liquid were pipetted into each of four nephelometer cups. The greatest precautions were taken to exclude dust, and all opperations with the nephelometer were performed in a room which had been unoccupied for six months previous to its use for this purpose, so that there was no possibility of contamination of the air with fumes of hydrochloric acid. To two of the tubes were made additions of 1cc. of a solution of silver nitrate containing 1mgm. silver per cc., and to the other two, 1cc. of a solution of calcium chloride containing an equivalent amount of chloride ion. The contents of each tube were then carefully mixed with stirrers, and

the solutions were allowed to stand for six hours under cover of earthenware jars to protect them from dust. This duplication of the nephelometric tests was performed to ensure the immediate detection of anomalous results, but it was unusual for there to be any contradiction between the two sets of nephelometer tubes. It was found that the difficulty in securing good agreement between them was greatest when the first preliminary determination of the atomic weight of the calcium extracted from rock was made, for in this instance a value of 40.075 was originally assumed, and comparatively large additions of chloride were necessary to raise it to the observed value of 40.090. Subsequently this value of 40.090 was assumed, and little difficulty was experienced in obtaining concordant readings with the two sets of tubes.

From the ratio of the lengths of the two columns required to produce equal apparent opalescence the amount of silver or chloride required to reach the exact end point was calculated, and this was added to the main liquid in the flask from a very dilute solution. After shaking for ten minutes the flask was again cooled in ice for twenty four hours and the procedure continued until the two columns of liquid gave equal opalescence to within a ratio of 98:100.

In general an average of three additions of either chloride or silver solution was sufficient to reach the point of equal opalescence in each of the two sets of tubes, and when this had been attained the volume of the liquid in the conical flask was measured. Knowing this volume, the total volume of liquid withdrawn during the nephelometric tests, and the amounts of additions of chloride and silver solutions, it was a matter of straightforward calculation to determine the small correction which had to be applied to the weight of silver or calcium chloride. The atomic weight of the calcium was obtained from the expression

$$A = \frac{215.76 \times w_1}{w_2} - 70.914$$

where

A = Atomic Weight of Calcium,

215.76 = 2 Atomic Weight of Silver,

70.914 = 2 Atomic Weight of Chlorine,

w_1 = Corrected weight of calcium chloride,

and w_2 = corrected weight of silver.

TYPICAL DETERMINATION.

The calcium chloride employed in this experiment was derived from sea-shells, the nitrate having been four times recrystallised.

Weight of calcium chloride in vacuo = 2.02806 gm.

Volume of nitric acid of a strength equivalent to 1mgm. Cl^- or .790mgm. CaO per 10cc., required to bring the chloride solution to the same degree of acidity as a solution of neutral calcium chloride. = 3.7c.c.

Weight of CaO in fused chloride = .00029gm.

Corrected weight of Calcium chloride in vacuo. = 2.02777gm.

Weight of silver in vacuo. = 3.94031

Weight of silver subsequently added from a dilute solution. = .00194 gm.

Total weight of silver added in vacuo. = 3.94224 gm.

1st. nephelometric test.

80c.c. liquid withdrawn.

Silver Nitrate.		Calcium chloride.	
A	B	A	B
60	60	36	38

3 c.c. of a calcium chloride solution, equivalent to 1mgm. silver per 10c.c., added to the main solution.

2nd. nephelometric test.

60c.c. liquid withdrawn.

Silver Nitrate.		Calcium chloride.	
A	B	A	B
57	58	60	60

·5c.c. silver nitrate solution, containing 1mgm. silver per 10c.c. added to main solution.

3rd. nephelometric test.

70c.c. liquid withdrawn.

Silver Nitrate.		Calcium chloride.	
A	B	A	B
61	59.5	60	59

Equality.

Final volume of solution = 1500c.c.

To 1570c.c., .5c.c. silver nitrate solution added.

to 1630c.c. should be added .52c.c. i.e. .00005gm. silver.

To 1630c.c., 3c.c. calcium chloride solution added.

to 1710c.c. should be added 3.15c.c. i.e. .00016 gm. calcium chloride.

Total weight of Calcium Chloride = 2.02793 gm.

Total weight of Silver = 3.94229 gm.

Atomic weight of calcium = 40.074

EXPERIMENTAL RESULTS:-

The values of the atomic weights of the calcium derived from the two sources are given below. The samples of chloride, marked A and B in both tables, were prepared from calcium nitrate which had been three and five times crystallised respectively, while the silver samples A and B were obtained from silver nitrate, six and eight times recrystallised.

Table I.

Calcium from Sea-Shells.

Sample of Chloride.	Sample of Silver.	Corr. wt. of Chloride.	Corr. wt. of Silver.	At. Wt.
	A	2.02793	3.94230	40.074
A	A	2.09760	4.07770	40.074
	B	2.23959	4.35369	40.075
	A	2.18660	4.25062	40.077
B	B	2.13950	4.15897	40.079
	B	2.04200	3.96947	40.079

Table II.

Calcium from Rock.

Sample of Chloride.	Sample of Silver.	Corr. wt. of Chloride.	Corr. wt. of Silver.	At.Wt.
	B	1.94278	3.77612	40.092
A	B	1.98782	3.86364	40.093
	A	1.88677	3.66715	40.095
	B	1.96884	3.82687	40.090
B	B	2.19803	4.27222	40.093
	A	2.17033	4.21850	40.090

The consistency of the results furnished strong evidence that the materials were pure, for it was most likely that the amount of any impurity which remained in the calcium nitrate from the third recrystallisation or in the silver nitrate from the sixth recrystallisation, would have been diminished sufficiently

during the further recrystallisations to have been evident by a variation in the atomic weight.

The final values for the atomic weights were calculated from the formula

$$R = 0.8453 \frac{\Sigma(+v)}{n(n-1)^{\frac{1}{2}}}$$

where R = probable error,

$\Sigma(+v)$ = sum of deviations of every possible error from the mean,

n = number of observations.

Calcium from Sea-Shells.

$$R = \frac{0.8453 \times .012}{6 \times \sqrt{5}} = .0008$$

Atomic Weight = 40.076 ± .0008

Calcium from Rock.

$$R = \frac{0.8453 \times 0.009}{6 \times \sqrt{5}} = .0006$$

Atomic Weight = 40.092 ± .0006

DISCUSSION:-

The atomic weight of calcium was determined in 1910 by Richards and Hönigschmid (loc. cit.), who obtained the values 40.070 and 40.074 from the ratios $CaBr_2$:2AgBr and $CaCl_2$:2Ag respectively. The latter value of 40.074 was suggested as most probably correct. A reinvestigation in 1931 by Hönigschmid and Kempter (loc. cit.), gave the value 40.084, but the result of 40.076 obtained in the present research closely confirms the earlier figures of Richards and Hönigschmid.

During the purification of a calcium derived from sylvine , Hönigschmid and Kempter showed that repeated precipation as oxalate was the only effective means of removing strontium, and as the value, 40.076, was obtained with a calcium which had been purified in this way, it seems certain that this figure is correct. The somewhat high result obtained by Hönigschmid and Kempter might in the first place be due to the presence of a small amount of strontium which had not been removed by the repeated crystallisations of calcium nitrate, or on the other hand it might be ascribed to the existence of Ca_{41} isotope in the marble which was employed as starting material. Allison, by his magneto-optic method, detected Ca_{41} in only six of the fourteen commercial calcium salts he examined, thereby proving that in these six cases

at least, the calcium must have been at some time in close contact with potassium. It is therefore possible that at some geological period before the formation of the marble which yielded the atomic weight of 40.084, the calcium content had been associated with potassium and had thus acquired a certain percentage of Ca_{44}, the percentage depending both on the relative amounts of calcium and potassium, and on the duration of the association. The high atomic weight of the calcium from this source might therefore have been due to the presence of Ca_{44}.

The sylvine calcium of Hönigschmid and Kempter gave an atomic weight of 40.093, and as the rock calcium gave a value of 40.092 the increase above the normal cannot be due to experimental error. It was shown spectroscopically by Ruthardt, (Zeit. fur. Anorg. Chem. 195, 15, 1931) that the sylvine calcium did not contain strontium in sufficient quantity to affect the atomic weight by .002, and it is thus most unlikely that the rock calcium contained a greater amount of impurity. It is intended to show in a further investigation that barium and strontium, after deliberate addition to calcium, can be completely removed by repeated precipitation as oxalate.

Accepting for the moment that barium and strontium were absent from the pure rock calcium,

the increase in the atomic weight above the normal must be ascribed to Ca_{41}, and this has a great significance, as it enables tentative figures for the half-period of potassium to be put forward. The half-period may be obtained from the expression

$$\lambda = \frac{-2.303 \times 0.693 \times t}{\log_{10}\left(-\frac{w}{0.067 \times 7.77} + 1\right)}$$

where t = age of rock

(0.067×7.77) = amount of K_{41}, (as the rock contains 7.77% potassium, and potassium contains 6.7% K_{41}), and

where w can be obtained from the equation

$$A = \frac{(0.20 - w)\ 40.076 + 41w}{0.20}$$

in which A = atomic weight of the calcium

and 40.076 = atomic weight of "average modern calcium"

It was pointed out that during the treatment of the rock with hydrochloric acid approximately 30% of the total calcium content was extracted and that this amount increased only very slowly after four hours treatment. If it is assumed that all of the Ca_{41} is extracted then A, the atomic weight of the total calcium in the rock, becomes $40.076 + \frac{1}{3}(40.092 - 40.076)$ and the value for the half period may be calculated as approximately 2×10^{12} years.

If on the other hand it is assumed that the extracted calcium has the same isotopic composition

as the calcium remaining behind in the extracted residue the half-value period of K_{41} is reduced to approximately 7×10^{11} years.

These tentative values for the half-period tend to support the estimate, 1×10^{12} years, of Hevesy, and to discredit Holmes and Lawsons figure of 7.5×10^{10} years. It should be noted that if the increase above the normal atomic weight were in part due to the presence of a trace of strontium, the value for the half-period would become even greater than 7×10^{11} years.

In view of the complexity of the research and of the great necessity of obtaining confirmation of the atomic weights of "average modern" and "heavy" calcium an independent research was undertaken by Mr. W. W. Smith. A Pegmatite, the age of which was estimated by geologists to be about 6×10^{8} years, was brought from Portsoy to provide a source of "heavy" calcium. The ordinary calcium for this research was extracted from Bermuda Limestone.

The atomic weights of these two samples of calcium are in close agreement with the results obtained from sea-shell and Rhiconich-rock calcium and provide further strong evidence of the existence of Ca_{ω} in very old potassium-rich rocks. They also support the suggestion that the normal calcium

of Hönigschmid and Kempter contained either Ca_{41} or traces of strontium impurity.

TABLE 3.

Source of Calcium	Atomic Weight	Limits of half-value period of K_{41}
Sea shells	40.076	
Bermuda Limestone	40.077	
Rhiconich rock	40.092	2×10^{12} — 7×10^{11} yrs.
Portsoy rock	40.089	1.3×10^{12} - 4.3×10^{11} yrs.